An iterative model-free method to determine the activation energy of non-isothermal heterogeneous processes

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ABSTRACT

A new iterative model-free (isoconversional) method with integration over a given range of conversion for determination of the activation energy using non-isothermal data recorded at several heating rates has been suggested. The advantages of applying this method in comparison with often used linear and nonlinear isoconversional methods are put in evidence. The suggested method was applied to experimental non-isothermal data for degradation of polyvinyl chloride, decomposition of ammonium perchlorate and crystallization of poly(ethylene terephthalate) melt. The so obtained values of the activation energy were compared with those resulting from other methods of analysis.

1. Introduction

Under non-isothermal conditions at a linear heating rate, the kinetics of heterogeneous reactions is usually described by the rate equation:

$$\frac{d\alpha}{dt} \equiv \beta\frac{d\alpha}{dT} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \qquad (1)$$

where α is the degree of conversion, t is the time, T is the temperature, β is the linear heating rate, A is the pre-exponential factor, E is the activation energy, $f(\alpha)$ is the differential function of conversion and R is the gas constant.

Starting with this equation, various procedures for evaluating the kinetic triplet (A, E, $f(\alpha)$) were developed. As has results from some critical analyses [1–14], the correct determination of non-isothermal kinetic parameters involves the use of experimental data recorded at several heating rates. These data have allowed applying the isoconversional (model-free) methods in assessing the activation energy on the conversion degree that can be correlated with the investigated process mechanism. Isoconversional procedures are classified as either linear or nonlinear. In the linear procedures, from which we mention Friedman (FR) [15], Flynn–Wall–Ozawa (FWO) [16,17], Kissinger–Akahira–Sunose (KAS) [18], Li–Tang (LT) [19,20], the activation energy is evaluated from the slope of a straight line, while in integral [21–25] and differential [26] nonlinear procedures the activation energy is evaluated from a specific minimum condition.

Both linear and nonlinear procedures may be either differential or integral according to the equation that underlies them, namely Eq. (1) or its integral form:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} \equiv g(\alpha) = \frac{A}{\beta}\int_0^{T_\alpha}\left[\exp\left(-\frac{E}{RT}\right)\right]dT \equiv \frac{A}{\beta}I(E_\alpha, T_\alpha) \qquad (2)$$

where $g(\alpha)$ is the integral conversion function and $I(E_\alpha, T_\alpha)$ is the temperature integral that cannot be exactly resolved.

The linear methods use some simple approximations of the temperature integral, like those suggested by Doyle [27] and Coats and Redfern [28], which exhibit a relative low accuracy. On the other hand, the integral nonlinear procedures allow using more precise approximations of this integral, like the rational expressions given by Senum and Yang [29]. Therefore, the application of integral nonlinear procedures leads to accuracy values of E. However, in comparison with linear methods, the use of nonlinear methods need a longer computational time. An attempt to outrun this disadvantage was performed by Gao et al. [30] who suggested an iterative procedure in which is assumed the reaction order model.

The derivation of equations that underlie the integral linear or nonlinear procedures assumes the independence of the activation parameters (E and A) on the conversion degree. On the other hand, it was pointed out [3,31–34] that when E depends on α, some important differences exist between E values determined by differential and integral isoconversional methods. In such a case, the differential isoconversional methods, like FR [15] and nonlinear differential [26] methods, as well as the modified (advanced) nonlinear method suggested by Vyazovkin [24] are recommended as the results obtained by integral isoconversional methods are dependent on the history of the system in the range $0-\alpha$ [4]. For

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some cases in which activation energy changes with conversion degree, the dependence of E_α on lower limit of integral was also put in evidence [35] by applying LT method.

Because differential methods employ instantaneous rate values, it is sensitive to inherent noise and tends to be numerically unstable [36]. The corresponding errors could be reduced by smoothing of the experimental data. In order to eliminate this systematic error, Vyazovkin [24] suggested a modification of the integral nonlinear method previously worked out by him [21], which consists in determining the integral $I(E_\alpha, T_\alpha)$ over a small $\Delta\alpha$ range (modified nonlinear method). Budrugeac [26] pointed out that for $\Delta\alpha \to 0$, the E_α values obtained by this method are practically equal to those obtained by FR method. Recently Cai and Chen [37] suggested a iterative linear integral isoconversional method for E_α evaluation that also uses the integration over a small $\Delta\alpha$ range and leads to correct values of the activation energy in much less time than Vyazovkin method.

In this paper, a new iterative integral isoconversional method with integration over a given range of conversion will be suggested. It will pointed out the following advantages of this method: the applicability for large and small $\Delta\alpha$ ranges; the possibility of using of precise approximations for temperature integral, even the values of this integral obtained by numerical integration performed by Mathematica software system; put in evidence the importance of lower limits of integration for E_α evaluation when E depends on α; the method can be applied even when the initial temperature corresponding to $\alpha = 0$ is randomly choice from the range 0 – minimum onset temperature; the application of this method in certain favorable cases could indicate the range of conversion degree in which the kinetics of the complex investigated process is determined by a certain step characterized by activation parameters that do not depend on α.

2. Theoretical part

The integration of Eq. (1) for the limits $\alpha_1(T_1)$ and $\alpha_2(T_2)$, and constant heating/cooling rate leads to:

$$g(\alpha_2) - g(\alpha_1) = \frac{A}{\beta} \int_{T_1}^{T_2} \left[\exp\left(-\frac{E}{RT}\right) \right] dT \tag{3}$$

In the integral linear isoconversional methods, as FWO [19,20] and KAS [21], as well as in nonlinear integral isoconversional method suggested by Vyazovkin [21], it is considered the case in which $\alpha_1 = 0$. In such condition, $\int_0^{T_1}[\exp(-E/RT)]dT \approx 0$ [38] and Eq. (3) turn into Eq. (2).

The integral temperature from the right member of Eq. (3) can be expressed as [25]:

$$I(E, T_1, T_2) = \int_0^{T_2} \left[\exp\left(-\frac{E}{RT}\right) \right] dT$$

$$- \int_0^{T_1} \left[\exp\left(-\frac{E}{RT}\right) \right] dT \equiv \frac{E}{R}[p(x_2) - p(x_1)] \tag{4}$$

where $x = E/RT$.

From the numerous approximations suggested for $p(x)$ in Section 3, we will use the four order approximation given by Senum and Yang [29], which exhibits a very high accuracy (the relative error lower than 0.6% for $x \geq 1$):

$$p(x) = \frac{e^{-x}}{x} \frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{5}$$

Eq. (3) can be written as:

$$g(\alpha_2) - g(\alpha_1) = \frac{AE}{R\beta}(T_2 - T_1)\left[\exp\left(-\frac{E}{RT_2}\right)\right] \frac{p(x_2) - p(x_1)}{(T_2 - T_1)\left[\exp\left(-\frac{E}{RT_2}\right)\right]} \tag{6}$$

from which it results:

$$\ln \frac{\beta}{T_2 - T_1} = \ln \frac{A}{g(\alpha_2) - g(\alpha_1)} + \ln R_I - \frac{E}{RT_2} \tag{7}$$

where $R_I = \frac{\int_{T_1}^{T_2}[\exp(-E/RT)]dT}{(T_2-T_1)[\exp(-E/RT_2)]} = \frac{E}{R} \frac{p(x_2)-p(x_1)}{(T_2-T_1)[\exp(-E/RT_2)]}$. Considering that $\alpha_1 = 0$, $T_1 = T_0$ (onset temperature of the considered process) and $R_I = 1$, this relation turn into:

$$\ln \frac{\beta}{T - T_0} = \ln \frac{A}{g(\alpha)} - \frac{E}{RT} \tag{8}$$

Eq. (8) was derived by Kennedy and Clark [39] by integration of rate Eq. (1) assuming T = const. and introducing in the obtained relation $\beta = T - T_0/t$. As was recently noted by Ortega [40] the derivation of Eq. (8) is conceptually erroneous because, in non-isothermal condition, the change of variable t with T must be performed before the integration of Eq. (1) considering T = const.

According to relation (7):

$$E = -R\frac{d\ln\left(\beta/(T_2 - T_1)\right)}{d\left(1/T_2\right)} - R\frac{d\ln R_I}{d\left(1/T_2\right)} \equiv E_{KC} - R\frac{d\ln R_I}{d\left(1/T_2\right)} \tag{9}$$

where $E_{KC} = -R(d\ln(\beta/T_2 - T_1))/d(1/T_2))$ is the activation energy corresponding to a procedure based on the relation:

$$\ln \frac{\beta}{T_2 - T_1} = \ln \frac{A}{g(\alpha_2) - g(\alpha_1)} - \frac{E}{RT_2} \tag{10}$$

This is similar with that derived by Kennedy and Clark [39].

In order to evaluate the activation energy using Eq. (9), the following iterative procedure is proposed:

  I. For R_I = const., by plotting $\ln(\beta/(T_2 - T_1))$ vs. $1/T_2$ activation energy $E^{(1)} \equiv E_{KC}$ is obtained from the slope of this straight line.
 II. $E^{(1)}$ being introduced in the expression of R_I, the value of $E^{(2)}$ is evaluated from the slope of the straight line $(\ln(\beta/(T_2 - T_1)) - \ln R_I)$ vs. $1/T_2$.
III. Let $E^{(2)}$ replace $E^{(1)}$ and repeat the step II until $|(E^{(i+1)} - E^{(i)})| \leq 0.1$ kJ mol^{-1}.

In comparison with integral isoconversional methods, like FWO and KAS methods, the above suggested iterative procedure exhibits the advantage of the possibility of using for temperature integral one of the more precise approximations or the values of this integral exactly numerically evaluated by Mathematica software system. Another advantage is that this procedure can be applied for all ranges of $\Delta\alpha$, even small $\Delta\alpha$ ranges.

Obviously, $E = E_{KC}$ for R_I = const. = C. In order to put in evidence the cases in which this condition is respected, we will consider that for relative small range of T_2 (in the experimental cases which will be analyzed in Section 3: $\Delta T_2 \leq 50$ K), the exact value of $I(E, T_2, T_1)$ is proportional with the following gross approximate expression of the temperature integral suggested by Mianowscki and Radko [41]:

$$I(E, T_2, T_1) \approx C^* I_{MR}(E, T_2, T_1) = C^* \left\{ T_2 \left[\exp\left(-\frac{E}{RT_2}\right) \right] \right.$$

$$\left. - T_1 \left[\exp\left(-\frac{E}{RT_1}\right) \right] \right\} \tag{11}$$

As we will show in Section 3, C^* value exhibits a relative standard deviation around the average value lower than 4%.

Substituting the expression (11) in the relation of R_I, the condition $R_I = C$ becomes:

$$T_2(C^* - C)\left[\exp\left(-\frac{E}{RT_2}\right)\right] + T_1\left\{C\left[\exp\left(-\frac{E}{RT_2}\right)\right] \right.$$

$$\left. - C^*\left[\exp\left(-\frac{E}{RT_1}\right)\right]\right\} = 0 \tag{12}$$